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Na_2O – B_2O_3 – ZnO – TiO_2 – SiO_2 GLASSCERAMIC MATTE COATINGS

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The dependence of the crystallizability of model glasses, when the coatings made from them are fired, on their thermal history is determined. The mechanism for obtaining coatings with different degrees of luster by directed crystallization is also determined. The general laws and particulars of phase transformations in Na_2O – B_2O_3 – ZnO – TiO_2 – SiO_2 glass that make it possible to control the crystallization process and design glassceramic matte coatings with prescribed physical – chemical and technological properties are determined.

A topical problem of modern materials science is the development of new glasses and glassceramic materials with a prescribed complex of physical – chemical and usage properties. Effective development of this important direction of scientific research will make it possible to solve complex, often unconventional, problems concerning the synthesis of high-strength, optically transparent (in a wide range of wavelengths), heat-resistant, chemically stable, durable, and biocompatible glassceramic materials and coatings based on them.

The best known results in the field of synthesis of glassceramic materials were obtained in the USA (Corning Incorporated), Germany (Shott), Japan (NEG), Russia (D. I. Mendeleev Russian Chemical Engineering University), and Belarus (Belarus State Technical University) [1, 2]. In Ukraine there are a number of institutes and enterprises which are working on the solution to these problems [3, 4]. However, the existing results concern primarily the production of glassceramic materials and, to much lesser extent, coatings.

Even though many theoretical studies have been performed and many compositions of glassceramic materials have been developed, the development of such low-melting materials and, especially, coatings based on them with short-time firing remains a difficult problem. The existing advances in the development and application of glassceramic coatings concern mainly the protection of large chemical apparatus made of thick-sheet steel.

At the same time, because the architectural-construction and medical industries and the production of household appliances and heating equipment are undergoing rapid development it is necessary to develop glassceramic protective coatings, formed under conditions of short-time firing and possessing high performance characteristics, on steel articles.

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Thus, universal protective-decorative glass coatings with high aesthetic-decorative characteristics, among which matte glassceramic coatings have a special place in the architectural-construction industry (fabrication of metallic facing for tunnels, above- and below-ground subway stations, railroad and bus stations, various production enclosures, medical boxes and operating rooms, design of buildings) [5, 6].

The objective of our work is to develop the principles of low-temperature synthesis of glassceramic matte coatings and determine the technological parameters for obtaining such coatings for enameling articles made of thin-sheet steel.

The required performance properties of existing glassceramic materials are attained by controlled phase-formation via the use of multistep high-temperature and prolonged regimes of heat-treatment of the initial glasses. To a certain extent, this can also concern glassceramic coatings obtained on chemical apparatus made of thick-sheet rolled carbon structural steels with multiple operations of firing of the bottom and cover glassenamel layers, the duration of each operation being 40 – 60 min. The required crystalline phases responsible for the thermal and chemical stability are formed, using such a technology, in multilayer coatings. The formation of glassceramic coatings on articles made of thick-sheet steel must be accompanied by the formation of crystalline phases during firing for several minutes.

To obtain low-melting matte glass coatings it is necessary to choose a glass-forming system where liquation and crystallization processes can proceed effectively in 3 – 10 min at relatively low firing temperatures (800 – 840°C). These processes can be controlled by changing the content of the components in this system. The system Na_2O – B_2O_3 – TiO_2 – ZnO – SiO_2 meets these requirements, since the simultaneous presence of titanium and zinc oxides in this system makes it possible to regulate the character of the formation and growth of nucleators.

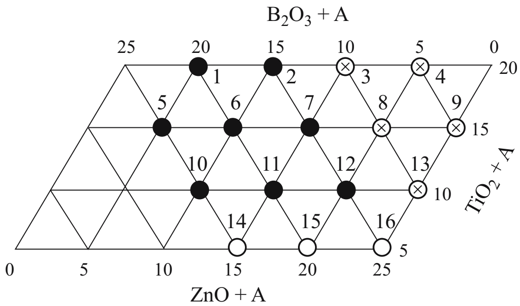


Fig. 1. Region of experimental compositions in the pseudoternary system (TiO_2 + A) – (B_2O_3 + A) – (ZnO + A), where A = Na_2O + SiO_2: ●) opaque lustrous; ○) transparent lustrous; ⊗) opaque matte.

The thermal history of the initial glasses must play a special role in these coatings because the crystal phase forms over a short period of time. Consequently, the crystallization processes occurring during glass making and cooling were studied and the mechanisms of the phase formation during the formation of matte coatings in low-carbon enameled steels were determined.

In choosing the compositions of the glasses to be used as the base for matte coatings with different crystallization tendencies, it was necessary to determine the region of glass formation in the indicated system and the compositions in it that would correspond to the following requirements for their properties:

the CLTE must be in the range $(90 - 110) \times 10^{-7}$ K^{-1} to match the CLTE of the bottom and cover enamels;

the surface tension must range from 220 to 240 mN/m, which is characteristic for titanium cover enamels;

the firing temperature must not exceed 840°C.

In this system, iso-lines of the properties which are responsible for the formation of a defect-free enamel coating on a metal substrate were constructed by simplex planning of an experiment. The Sheffe simplex-lattice plan for a studying a local section of the composition – properties diagram, making it impossible to distribute the experimental points over a $(q - 1)$-dimensional simplex uniformly, was chosen as the computational algorithm.

The method of planning an experiment was used to determine the region in the pseudoternary system (TiO_2 + A) – (B_2O_3 + A) – (ZnO + A), where A = (15Na_2O + 45SiO_2), with content 5 – 20%[2] TiO_2, 5 – 25% B_2O_3, 5 – 25% ZnO. Sixteen compositions of model glasses were synthesized in this region and their glass-forming capacity was investigated. It was established that transparent lustrous, opaque lustrous, and opaque matte glasses can be obtained in the pseudoternary system studied (Fig. 1).

To determine the characteristic features of crystallization during heat treatment of the experimental titanium-containing glasses, it was desirable to study by means of differential-thermal analysis the influence of their composition on the intensity of phase formation. The thermograms of glasses with < 25% ZnO and 10 – 20% TiO_2 have a substantial area with an endothermal effect, which precedes the exothermal effect of crystallization and characterizes the probability that a substantial number of crystalline nuclei will form (Fig. 2, thermogram *1*). The area of the endothermal effect in these glasses is larger than in glasses with 25% ZnO and similar content of TiO_2 (Fig. 2, thermogram *2*), which suggests that zinc oxide has a substantial effect on the crystallization processes in these glasses.

The sharply expressed peaks due to exoeffects in the thermogram of compositions with < 25% ZnO attest to a high rate of crystallization in them, a result of which is the formation of a substantial number of small crystals. The presence of additional steep peaks due to exoeffects at temperatures 600 – 630°C indicates crystallization of a substantial amount of titanates in these glasses. Conversely, a smooth peak with a small slope is determined in the thermogram with 25% ZnO. This attests to slower crystallization,

[2] Here and below — mass content.

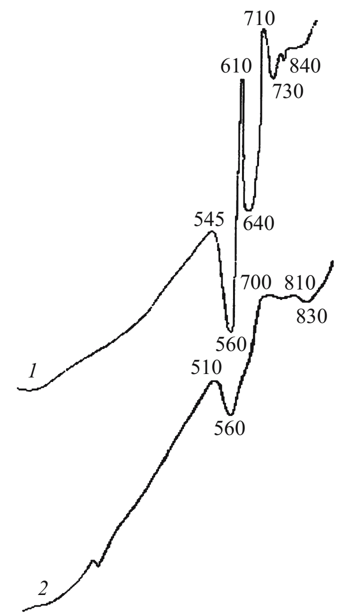
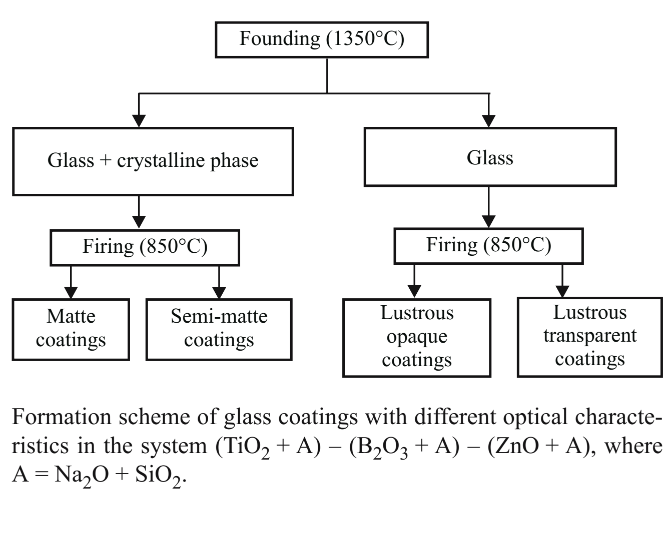


Fig. 2. Thermograms (°C) of frits with < 25% ZnO (*1*) and 25% ZnO (*2*).



Formation scheme of glass coatings with different optical characteristics in the system (TiO_2 + A) – (B_2O_3 + A) – (ZnO + A), where A = Na_2O + SiO_2.

which gives rise to the formation of large rutile crystals and serves as a prerequisite for the matte surface texture.

The temperature – time conditions for making the experimental glasses have a large effect on their crystallization process, and this effect is determined by the TiO_2 content. An investigation of the influence of the thermal history on the crystallization capacity of model glasses and on the optical characteristics of the coatings made from such glasses after firing showed that glass with ≤ 10% TiO_2 after founding are x-ray amorphous, while glasses with > 10% TiO_2 are characterized by the presence of a crystalline phase. When the coatings are fired, a further increase in the size of existing rutile crystals occurs and new crystals — zinc orthosilicate and zinc orthotitanate — appear. Since the ZnO content > 20% in the corresponding coatings, the number of TiO_2 crystal increases further, as a result of which the coating lose their luster. X-ray phase analysis established that the transformation of the crystalline phase in the experimental system occurs according to the following scheme:

$$Na_xTiO_2,\ SiO_2 \xrightarrow{600-780^\circ C}$$
$$TiO_2\ (\text{anatase}),\ Zn_2TiO_4 \xrightarrow{780-850^\circ C}$$
$$TiO_2\ (\text{rutile}),\ Zn_2TiO_4,\ Zn_2SiO_4.$$

The results obtained revealed a dependence of the crystallization power of the model glasses on their thermal history and showed that coatings with different degrees of luster can be obtained by directed crystallization according to the scheme proposed.

In summary, four groups of coatings were obtained on the basis of model glasses: transparent lustrous, opaque lustrous, opaque semi-matte, and opaque matte.

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